

## EXPERIMENTAL INVESTIGATION ON THE SELF-HEATING AND DECOMPOSITION OF TETRAFLUOROETHYLENE IN A 100-DM<sup>3</sup>-REACTOR

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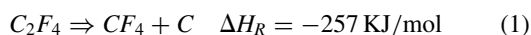
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In the industry there is a lack of data on the Minimum Ignition Temperature of decomposition of tetrafluoroethylene in industrial sized equipment. In order to determine the Minimum Ignition Temperature of Decomposition of tetrafluoroethylene in large scale vessels, a facility was designed and constructed. Tests were carried out in a cylindrical reactor with a volume of 100 dm<sup>3</sup> with initial pressures of 5 and 10 bar(a). In agreement with previous experiments with small scale cylindrical vessels, the Minimum Ignition Temperature of Decomposition of tetrafluoroethylene was observed to decrease with the initial pressure. The current paper describes the test setup and summarizes the experimental results achieved. The effect of the reactor adjustment (vertical or horizontal) is discussed. Moreover, simplified equations from the Semenov thermal explosion theory are used to attempt extrapolations of previous and current data on the Minimum Ignition Temperature of Decomposition of tetrafluoroethylene to other initial pressures and vessel volumes.

### INTRODUCTION

Tetrafluoroethylene (TFE, chemical formula C<sub>2</sub>F<sub>4</sub>) is a flammable gas, meaning it can form explosible mixtures with air. Furthermore, TFE is also chemically unstable since under certain circumstances the double bond connecting the carbon atoms can break releasing a high amount of energy. For the decomposition of TFE the presence of an oxidant is not required. TFE is produced at industrial scales with an annual production of about 80.000–90.000 tons and is employed as monomer in the production of polytetrafluoroethylene (PTFE, aka. as Teflon<sup>®</sup> resin by DuPont) and of copolymers. The process leading to the formation of PTFE and of copolymers normally occurs in large reactors as a liquid phase reaction. Under certain conditions of pressure and temperature the gas phase -mainly composed of TFE- above the liquid may undergo a self-heating, which might turn into a runaway reaction leading to the decomposition of TFE into tetrafluoromethane and carbon black (soot). This decomposition is strongly exothermal and has an explosive behavior (Duus, 1955) and can therefore lead to serious accidents (Daikin Industries LTD., 2004; Reza, 2007). Equation (1) shows the decomposition reaction:



Furthermore, under operational pressures TFE starts a dimerization forming octafluorocyclobutane (OFCB) already from temperatures of about 200°C, according to equation (2). The reaction rate increases with increasing pressure and temperature (Lacher, 1952; Babenko, 1993). During the industrial production of PTFE, the equilibrium might be shifted in the forward direction, thus energy would be released and the dimerisation reaction could act as a precursor of the explosive decomposition.



Gases like TFE, which can decompose without the presence of oxygen, are commonly called chemically

unstable gases. The so-called Minimum Temperature of Decomposition (MITD) is a safety characteristic which helps in assessing the hazards of this kind of gases. This is defined as the lowest temperature of a hot surface, e.g. the vessel walls, at which self-ignition for the decomposition of a chemically unstable gas like TFE occurs without the presence of an oxidizer like air. The MITD is therefore analogue to the standard Auto Ignition Temperature (AIT aka. MIT) for flammable gases, which represents the lowest temperature of a hot surface, where the most ignitable mixture of a flammable gas with air may register an ignition (DIN EN 14522, 2005 or ASTM E 659-78, 2005).

With the aim of understanding the conditions necessary to trigger TFE decomposition in large scale reactors, experiments for the determination of the MITD were performed in a cylindrical vessel of 100 dm<sup>3</sup> in volume. The effect of the vertical or horizontal adjustment of the reactor was studied. Tests at initial pressures of 5 and 10 bar(a) were carried out.

The current paper describes extensively the experimental setup and summarizes the results obtained. The collected data are discussed and compared with findings from previous studies with laboratory scale equipment. Furthermore, methods for the extrapolation of the MITD of TFE to other test conditions (initial pressures or vessel dimensions) are shown.

### EXPERIMENTAL SETUP

A schematic view of the experimental facility is shown in Figure 1. The core of the facility was a cylindrical stainless steel vessel (material number 1.4571). The reactor had a volume of 100 dm<sup>3</sup> and a pressure resistance of 345 bar(a) at ambient temperature and was dimensioned according to the calculation methods proposed in DIN EN 13445-3 (2002) and VDI 2230 (2003) for unfired pressure vessels. Tests were performed in an explosion bunker, in order to

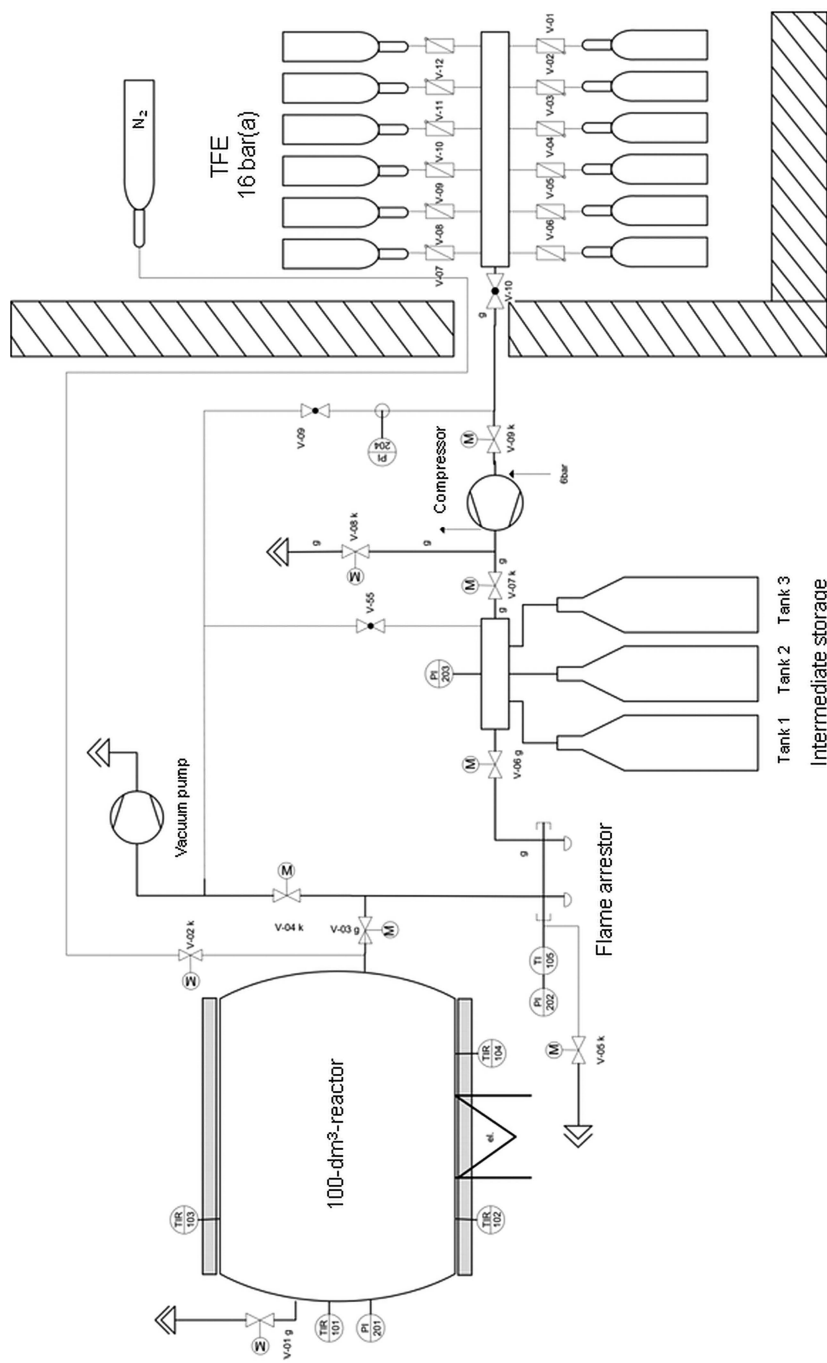
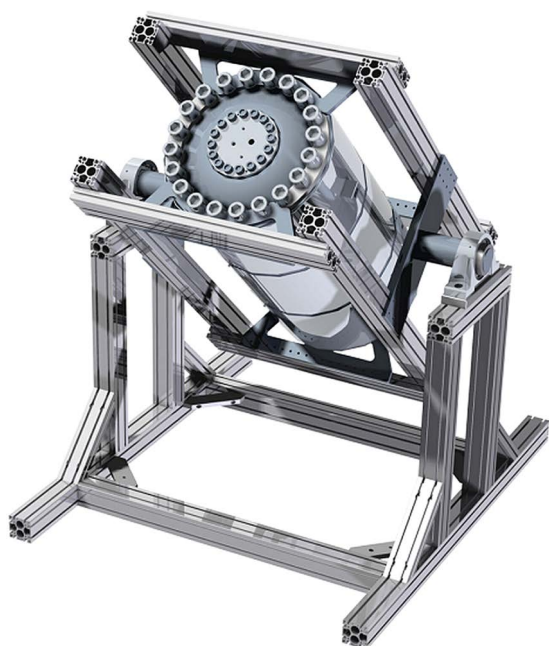


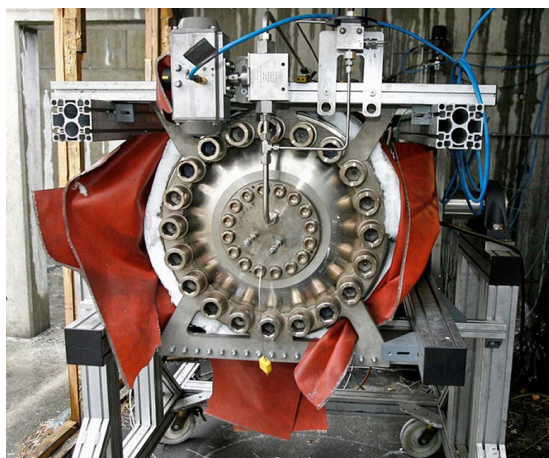
Figure 1. Schematic view of the experimental facility.



**Figure 2.** 100-dm<sup>3</sup>-vessel mounted on the support (3D-CAD view).

operate under safe conditions. Up to 12 TFE supply cylinders were located in a separate bunker. The operating board as well as the gas supply was run from a separate control room, where also the data acquisition system was located.

The 100-dm<sup>3</sup>-vessel was mounted on a special support, which allowed a complete 360° rotation (see Figure 2) so that effect of the orientation on the MITD of TFE could be studied. A top view of the reactor can be seen in Figure 3. For practical purposes a lid-in-lid system was used on both sides of the reactor: the smallest lids could be easily removed for the cleaning of the vessel,



**Figure 3.** Top view of the reactor in the horizontal position.

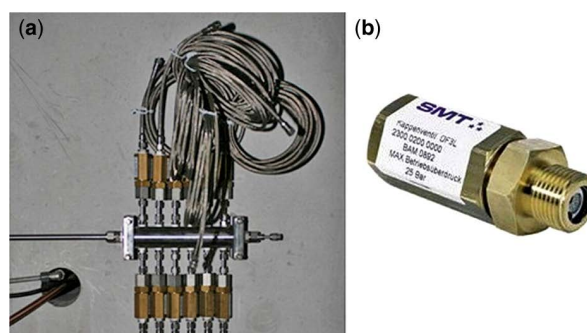
since the removal of the main reactor caps would have been unpractical.

Three 50-dm<sup>3</sup>-cylinders each with a pressure resistance of 300 bar(a) were used to store TFE before the experiment (tank 1–3 in Figure 1). This was necessary in order to achieve short filling times of the autoclave (under 40 s) and thus to reduce pre-reactions during the fill-up of the vessel. By this intermediate storage the risk of a back ignition in the original supply cylinders was also strongly reduced.

With the aim of avoiding the possibility of a back reaction towards the intermediate storage in case of an accidental ignition during the fill-up of the autoclave and therefore to protect the whole installation, a flame arrester was inserted in the pipeline between the reactor and the cylinders for the intermediate storage as a further safety measure. The flame arrester consisted of a 0.6 m long tube, whose interior was filled with pipes of small diameter. Moreover, the flame arrester was equipped with two rupture discs, in order to release the pressure build-up, which originates during the decomposition of TFE.

A compressed air-driven compressor (company: Maximator) was employed to reach the required pressures for the filling of the intermediate storage cylinders. The compressor was activated from the operating board and used the discharged air for cooling the working piston, so it was not subjected to over-heating. The built-in non-return valves of the compressor provided a stop for the flow in the event of a back reaction due to TFE ignition. A special distribution device mounted in the separate supply bunker allowed for the connection of up to 12 cylinders (Figure 4a). A safety device was inserted in each supply line as a redundant preventive measure (Figure 4b). This device consists of an automatic acting shut-off system, a flame arrester and non-return valve and had been previously tested successfully for stopping the propagation of TFE decomposition in the pressure range needed.

The whole facility was remote controlled via two-way pneumatic ball valves, actuated from the operating board and driven by compressed air at 6–8 bar(a). The valves are made of high-alloyed steel (material number 1.4401), which is long term resistant against corrosion and inert against TFE. In the TFE supply pipeline to the reactor and



**Figure 4.** Connections for the TFE supply cylinders (a) and detail of a single safety device (b).

in the exhausts pipeline valves with an orifice diameter of 12 mm were mounted, indicated with a “g” in the schematic view in Figure 1 (e.g. V-03 g). The supply line for nitrogen, used for purging the reactor after an ignition, and the discharge line for fresh TFE were equipped with ball valves with an orifice diameter of 4 mm, marked with a “k” in Figure 1 (e.g. V-04 k). Both valve types can withstand high pressure and temperature. A vacuum pump (company: Edwards) was used to partially or completely evacuate the facility, when required.

The reactor was brought to the desired temperature by means of three heating jackets, which surrounded the vessel body and had a total power of 9 kW. In each heating jacket one platinum resistance thermometer Pt-100 was inserted to record the temperature, which was regulated by means of a self-made controller. In order to reduce heat losses to the surroundings as much as possible, a double-layer insulation was used: the first layer was made of glass wool, which was then in turn enveloped in a glass fibre pad for protection against adverse weather conditions. The insulation is shown in Figure 3, where the material covering the reactor lid was removed for clearness while shooting the picture.

Inside the reactor the temperature was measured by three 1.5-mm-NiCr/NiAl-thermocouples (K type). Piezoresistive transducers (company Keller, type PA-10) were used to measure the pressure in the reactor, in the flame arrestor, in the intermediate storage cylinders, and in the pipeline between the gas supply cylinders and the compressor.

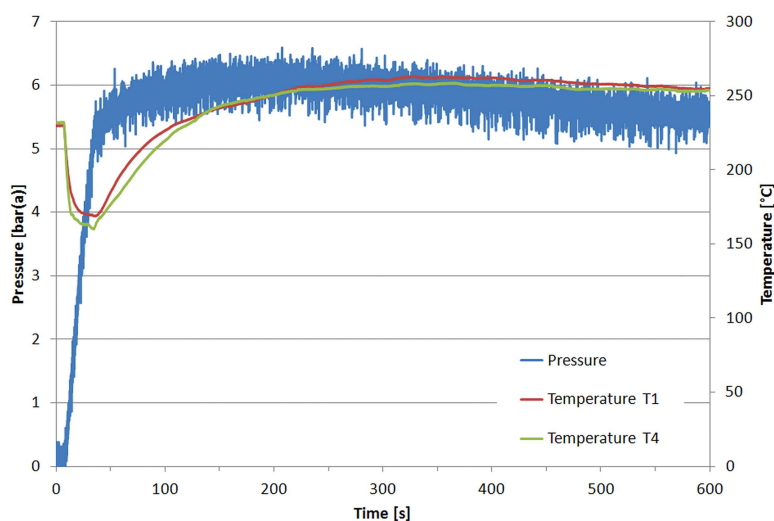
The pressure transducers were calibrated by means of a precision calibrator (company: Druck, type: DPI + 515, accuracy of 0.01% FS) and had a maximum error of 0.25% FS. The temperature and pressure signals were sent to an A/D-converter (company Jet Systemtechnik GmbH, type MCL-USB, 16 channels 12 Bit A/D, overall sampling rate 500 kHz), so that the signals could be checked in real-time and stored as digital data.

## EXPERIMENTAL PROCEDURE

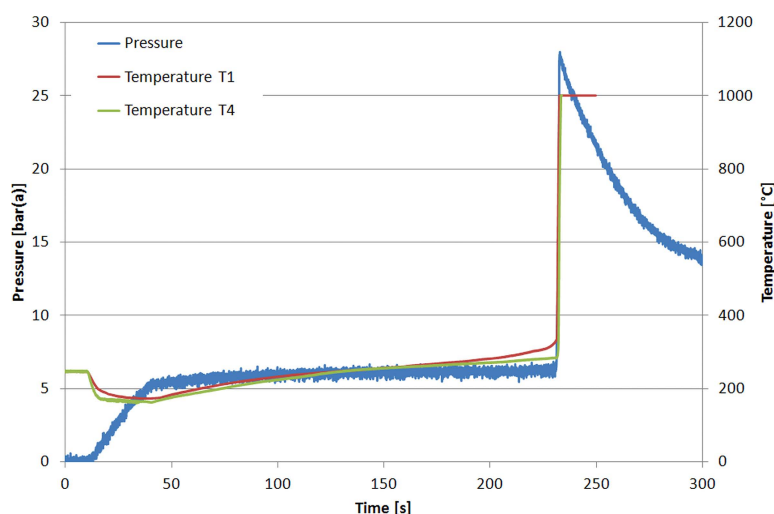
Preliminary leak tests of the whole system with nitrogen at high pressure had to be carried out prior to the first experiment. Once the facility had been proven leak-proof, nitrogen was discharged and then the system was evacuated via the vacuum pump. Thereafter, the intermediate storage cylinders were brought to the pressure required for the filling of the reactor by means of the compressor. Once this was complete, the line between the compressor and the intermediate storage cylinders was discharged by closing the valves V-07 k and V-10 and opening the valve V-08. By releasing TFE to 1 bar(a), the possibility of a back reaction from the storage cylinders to the compressor was reduced, since the decomposition of TFE is very unlikely to propagate at this pressure.

Once the reactor reached the set temperature, the data acquisition was started and TFE was led from the storage cylinders to the reactor through the flame arrestor by opening the valves V-03 g and V-06 g. Once the 100-dm<sup>3</sup>-vessel was filled with the test pressure, the valves V-03 g and V-06 g were closed. To further protect the intermediate storage cylinders in case of a back reaction from the reactor, the flame arrestor was then vented to atmospheric pressure by activating the valve V-05 k.

The temperature and pressure curves in the vessel were monitored in real-time from the control room over the whole test duration. The criterion for the onset of the decomposition was the appearance of temperature and pressure peaks in the recordings. If no reaction was observed within 30 min, the data acquisition was stopped and the vessel was discharged by operating the valve V-01 g. When further tests were required, it was then necessary to evacuate the reactor and the flame arrestor and to bring back the intermediate storage vessel to the needed pressure. Thereafter a new test could begin following the same procedure as described previously.



**Figure 5.** Temperature and pressure recordings in a test with a real initial pressure of 6.18 bar(a) and a wall temperature of 250°C (10 K under the MITD). Vessel vertically orientated.



**Figure 6.** Temperature and pressure recordings in a test with a real initial pressure of 6.22 bar(a) and a wall temperature of 260°C (MITD). Vessel vertically orientated.

When a decomposition was detected, the heating jackets were shut off and to allow the temperature and pressure to reduce to acceptable values. Then reactor was discharged to atmosphere, purged with nitrogen and was left to cool down for nearly 24 hours. Afterwards the vessel could be opened for cleaning. The O-ring seals were replaced if needed, the reactor was sealed and further leak tests were performed. The heating jackets were then switched on: generally, it took about 12 hours to reach the set temperature. Provided the pressure in the intermediate storage vessel was sufficient, a further test could then begin. Otherwise, these had to be refilled to the required pressure via compressor.

To determine the MITD of TFE for each initial pressure, the reactor wall temperature was varied in  $\pm 10$  K steps to find the lowest temperature at which an ignition occurred. A non-ignition had to be validated with three tests with the same wall temperature (10 K under the MITD).

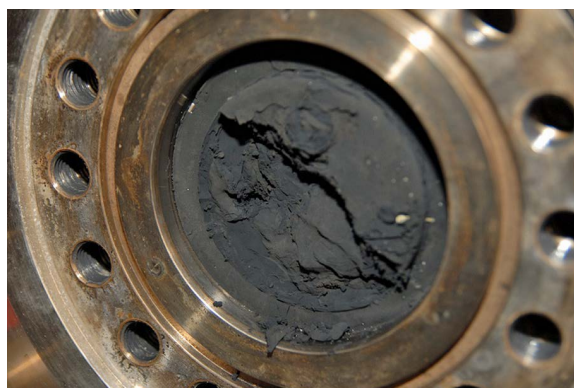
## RESULTS AND DISCUSSION

During the filling of the reactor cold TFE from the intermediate storage vessels was injected and the thermocouples registered lower values than the wall temperature. Since the TFE supply to the vessel was stopped the moment the data acquisition system registered the set pressure, a higher amount of gas than required was filled. Therefore, considering the gas at the set temperature the real initial pressure in the autoclave would be actually higher than the set pressure. This effect is not negligible in large vessels and had to be accounted for. At high temperatures TFE behaves as an ideal gas, thus the ideal gas law was used to determine the real initial pressure. Real initial pressures of about 6 bar(a) and 11 bar(a) for set pressures of 5 bar(a) and 10 bar(a), respectively, were calculated.

Figure 5 shows the typical recordings in an experiment without TFE ignition (initial conditions: set pressure 5 bar(a),

real pressure 6.18 bar(a), wall temperature 250°C). After the filling the pressure shortly increased due to heating of the injected cold gas and then dropped due to the reduction in the number of moles caused by the dimerisation of TFE into OFCB (equation 2). The heat produced by the dimerisation was dispersed to the surrounding and therefore no ignition occurred. For higher wall temperatures the energy released by the dimerisation exceeded the heat losses and the decomposition of TFE was initiated, as shown in Figure 6 (initial conditions: set pressure 5 bar(a), real pressure 6.22 bar(a), wall temperature 260°C). The peaks in the temperature and pressure curves due to the exothermal release by the decomposition are clearly visible in the picture. It can be furthermore noticed that a certain time is needed for the onset of the decomposition. This is the so-called Ignition Delay Time (IDT), which has been confirmed to shorten with increasing wall temperature in the experiment performed.

The decomposition reaction of TFE generated a large amount of carbon black (soot). Figure 7 shows a picture of



**Figure 7.** Soot accumulation near the reactor top after a test with ignition.

**Table 1.** Experimentally determined values of MITD of TFE in the 100-dm<sup>3</sup>-vessel.

| Set pressure<br>[bar(a)] | Vertical Orientation      |              | Horizontal Orientation    |              |
|--------------------------|---------------------------|--------------|---------------------------|--------------|
|                          | Real pressure<br>[bar(a)] | MITD<br>[°C] | Real pressure<br>[bar(a)] | MITD<br>[°C] |
| 5                        | 6.22                      | 260          | 5.71                      | 280          |
| 10                       | 10.94                     | 230          | 11.32                     | 240          |

the accumulation of soot in proximity of the reactor top. Usually, both the reactor top and bottom were filled with soot after a test with ignition.

In Table 1 the data on the MITD of TFE collected during the current experimental campaign are summarized. The MITD of TFE decreases with increasing initial pressure, in agreement with previous tests in small scale reactors with full or partial heating (BAM, 2005; Ferrero, 2012). The effect of the reactor orientation is also to be seen, since differences in the MITD of TFE of up to 20 K within the pressure range analysed were observed between the vertical and horizontal orientation. The effect of the reactor arrangement seems to decrease as the initial pressure increases. Anyway, tests at higher initial pressure would be required to confirm these finding.

The pressure influence on the ignition temperature can be represented by approximation presented in equation (3), according to the simplified theory on spontaneous thermal ignition from Semenov (Glassman, 1987).

$$\ln(p_0) = \frac{a}{\text{MITD}} + b \quad (3)$$

where:

a = constant obtained by fitting Eq. (3) to the experimental data [bar(a)\*K]

b = constant obtained by fitting Eq. (3) to the experimental data [bar(a)]

$p_0$  = real initial pressure [bar(a)]  
MITD = Minimum Ignition Temperature of Decomposition [K]

The results from the current work have been plotted in  $\ln(p_0)$  vs.  $1/\text{MITD}$  diagrams in Figure 8 for both vertical and horizontal orientations of the vessel. The equations corresponding to the Semenov approximation are presented in the graph. These equations can be rewritten in a more convenient form, in order to directly extrapolate the MITD to other initial pressures, as presented in the following equations:

$$\text{MITD} = \frac{a}{\ln(p_0) - b} - 273.15$$

general equation, MITD in °C,  $p_0$  in bar(a) (4)

$$\text{MITD} = \frac{5046}{\ln(p_0) + 7.640} - 273.15$$

100 dm<sup>3</sup> fully heated vessel, vertically orientated (5)

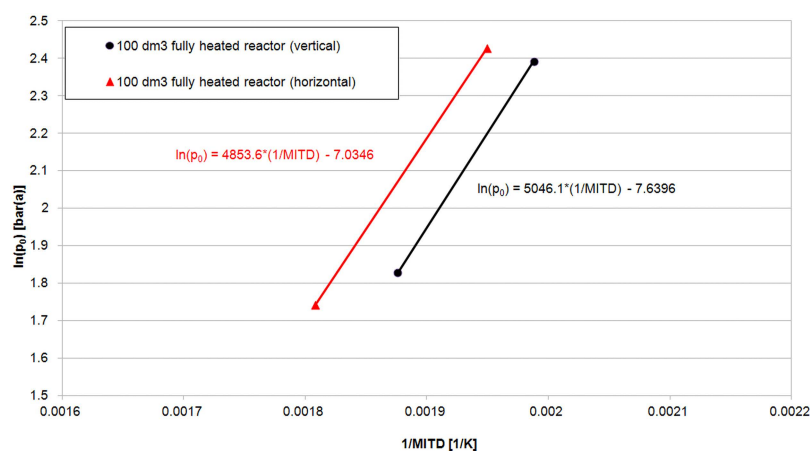
$$\text{MITD} = \frac{4854}{\ln(p_0) + 7.035} - 273.15$$

100 dm<sup>3</sup> fully heated vessel, horizontally orientated (6)

In Table 2 the MITD of TFE in the 100-dm<sup>3</sup>-vessel calculated by equations (5) and (6) for different initial pressures for both vertical and horizontal alignment of the 100-dm<sup>3</sup>-reactor are shown. The extrapolation in the table refers to a fully heated cylindrical vessel. It must be noticed that the approximations for the current study are generated with two experimental points and should be confirmed with MITD tests at higher initial pressures.

The Semenov approximation can also be applied to the dependence of the MITD with the vessel volume for a specified initial pressure according to the following equation:

$$\ln(V) = \frac{A}{\text{MITD}} + B \quad (7)$$



**Figure 8.**  $\ln(p_0)$  vs.  $1/\text{MITD}$  curves and approximation according to the Semenov theory.

**Table 2.** MITD of TFE for a fully heated 100-dm<sup>3</sup>-vessel at different pressures according to the Semenov extrapolation.

| Initial pressure<br>[bar(a)] | Vertical<br>Orientation | Horizontal<br>Orientation |
|------------------------------|-------------------------|---------------------------|
|                              | MITD<br>Semenov [°C]    | MITD<br>Semenov [°C]      |
| 2.5                          | 317                     | 337                       |
| 5                            | 272                     | 288                       |
| 10                           | 234                     | 247                       |
| 15                           | 215                     | 225                       |
| 20                           | 201                     | 211                       |

where:

A = constant obtained by fitting eq. (7) to the experimental data [dm<sup>3</sup>\*K]

B = constant obtained by fitting eq. (7) to the experimental data [dm<sup>3</sup>]

V = vessel volume [dm<sup>3</sup>]

MITD = Minimum Ignition Temperature of Decomposition [K]

In Figure 9 the data on the MITD of TFE from the current study and from previous works with small scale reactors (BAM, 2005; Ferrero, 2012) are plotted in a ln(V) vs. 1/MITD diagram. The points in Figure 9 refer to fully heated cylindrical vessels and allow for the determination of constants A and B of equation (7) for initial pressures of 5 and 10 bar(a). The volume dependence of the MITD can then be rewritten in the more convenient forms presented in the following:

$$\text{MITD} = \frac{A}{\ln(V) - B} - 273.15$$

general equation, MITD in °C, V in dm<sup>3</sup> (8)

$$\text{MITD} = \frac{22858}{\ln(V) + 38.219} - 273.15$$

5 bar(a), fully heated vessel, vertically orientated (9)

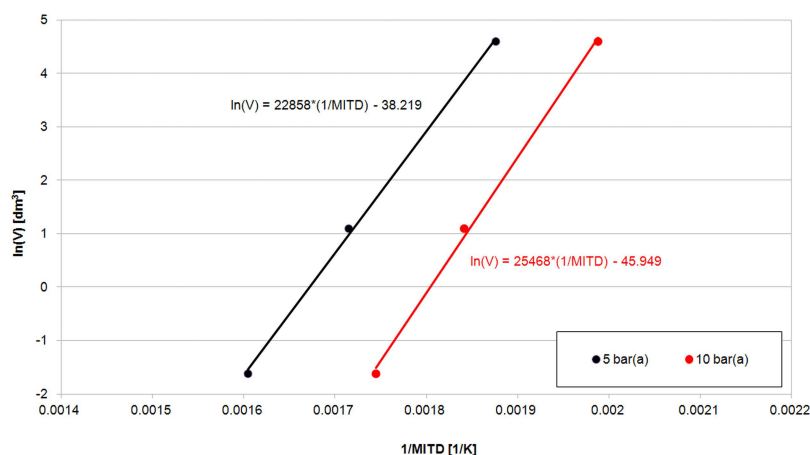
$$\text{MITD} = \frac{25468}{\ln(V) + 45.949} - 273.15$$

10 bar(a), fully heated vessel, vertically orientated (10)

As previously pointed out the real initial pressure in the tests with the 100-dm<sup>3</sup>-vessel were higher than the set values of 5 bar(a) and 10 bar(a). Since the MITD drops for increasing initial pressures, for the 100-dm<sup>3</sup>-vessel lower MITD values than the real ones were used for the Semenov approximation. This leads to an underestimation of the MITD if the equations are applied to larger volumes than the ones analyzed. From a safety related perspective a lower MITD means a more conservative prediction and this was considered acceptable. Therefore, the MITD of TFE for fully heated vertically orientated cylindrical vessels was extrapolated to larger volumes according to equations (9) and (10). Table 3 shows the MITD of TFE at 5 and 10 bar(a) for volumes up to 100000 dm<sup>3</sup> (100 m<sup>3</sup>).

## SUMMARY

An experimental facility was designed and assembled, in order to study the explosive decomposition of TFE at a large scale. Tests in a 100-dm<sup>3</sup>-reactor were performed, with the aim of assessing the Minimum Temperature of Decomposition (MITD) of TFE on hot walls at initial pressures of 5 and 10 bar(a). A decrease of the MITD of TFE with the initial pressure was detected, in agreement with previous data from laboratory scale experiments. The effect of the vertical or horizontal orientation of the reactor was studied, showing differences in the MITD of TFE of up to 20 K. The lower values of MITD were registered with the reactor in the vertical position, which probably promotes the formation of local



**Figure 9.** ln(V) vs. 1/MITD curves and approximation according to the Semenov theory.

**Table 3.** MITD of TFE for fully heated vessels of various volumes according to the Semenov extrapolation.

| Volume [dm <sup>3</sup> ] | MITD Semenov [°C] |           |
|---------------------------|-------------------|-----------|
|                           | 5 bar(a)          | 10 bar(a) |
| 0.2                       | 351               | 301       |
| 3                         | 308               | 268       |
| 100                       | 261               | 231       |
| 1000                      | 233               | 209       |
| 10000                     | 209               | 189       |
| 100000                    | 186               | 170       |

hot spots near the vessel top due to buoyancy effects. The influence of the autoclave arrangement seems to decrease as the initial pressure increases, at least in the pressure range analyzed. Furthermore, methods are presented for the extrapolation of the MITD of TFE to high initial pressures and large volumes. The work could therefore give advices for enhancing the safety in chemical reactors for TFE processing under elevated conditions.

#### SYMBOLS AND ABBREVIATIONS

|              |  |
|--------------|--|
| a            | constant of equation (3), bar(a)*K                     |
| A            | constant of equation (7), dm <sup>3</sup> *K           |
| b            | constant of equation (3), bar(a)                       |
| B            | constant of equation (7), dm <sup>3</sup>              |
| MITD         | Minimum Ignition Temperature of Decomposition, °C or K |
| $p_0$        | initial pressure in the vessel, bar(a)                 |
| V            | vessel volume, dm <sup>3</sup>                         |
| $\Delta H_R$ | heat of reaction, kJ/mol                               |

Table of unit conversions (if different from SI units)

| Physical quantity | Employed unit | SI unit | Conversion factor |
|-------------------|---------------|---------|-------------------|
| Mass              | ton           | kg      | 1 ton = 1000 kg   |
| Pressure          | bar/bar(a)*   | Pa      | 1bar = 100000 Pa  |
| Temperature       | °C            | K       | °C = K-273.15     |

\*bar(a) refers to absolute pressure.

#### ACKNOWLEDGEMENTS

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